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PCT/FP/00102

Process for cleaning articles METHOD FOR CLEANING OBJECTS

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[0001] This invention relates to a <u>process_method</u> for cleaning <u>articles_objects</u> and materials <u>made from ef metal</u>, glass, ceramics, plastic(s), or composites thereof or of textiles.

r00021 Cleaning processesmethods, in which a vapor produced by heating of an active cleaning liquid is brought into contact with articles to be cleaned the to-be-cleaned objects, are employed in the cleaning of a very wide variety of articles, such as metal articlesobjects, industrially-manufactured articlesobjects, such as printed circuit boards, articles of clothing, etc., to remove undesirable foreign substances of undesired contaminants, such as fats greases, lapping and polishing pastes, soldering pastes, adhesives, mixtures of inorganic (e.g., salinesalty) fouling substances and organic fouling substances (e.g., ones-consisting of fattygreasy residues), etc. Until recently, chlorinated hydrocarbons were typically used for such cleaning tasks. But now, because ofdue to their inadequatelack of environmental compatibility, and especially because offue to their ozone destruction potential, their carcinogenicity, and their toxic effect, theychlorinated hydrocarbons have been banned or use of them is allowed are usable only under very strictly defined conditions. One advantage of using chlorinated hydrocarbons was that such substances do not have noa flash point at commonly-occurring temperatures. Because of Due to the above-noted disadvantages, indicated they chlorinated hydrocarbons have been replaced by other hydrocarbons or solvents, such as polypropyleneglycol ethers, alcohols, acetone, and the likeetc. The latter have a flash points in the range of normally-occurring temperatures and are consequentlythus ignition hazardous. They also present another disadvantage in that they hardly remove pigment fouling or fouling withhaving ionic salts, since these solvents are very inefficient inonly poorly dissolvinge pigments and/or salts because ofdue to their ionic nature of the lattercharacter.

[0003] The object <u>of underlying</u> the invention <u>wasis</u> to <u>further</u> develop a <u>generic conventional</u> cleaning <u>processmethod</u> so that it is <u>performable</u> a <u>good cleaning effect may be achieved</u> in an environmentally compatible manner <u>while achieving a good cleaning effect</u>.

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[0004] Another object of the invention wasis to propareprovide a new cleaning process wherebymethod, by which mixtures of inorganic and organic fouling maycan be eliminated simultaneously removed in an efficient manner. Another additional object of the invention was represented by proparationis to provide of a processmethod for cleaning objects and materials made of metal articles and materials which is not as harsh in the results of its operation as are state of the art processes that acts more gently than previously known methods.

[0005] The <u>previously-identified</u> objects referred to above—are attained by a processmethod having the features specified inof patent Gclaim 1-of the patent. Advantageous developments embodiments of the process claimed for the invention are presented inventive method are found in patent Gclaims 2 to 19.

[0006] According to the invention, Agreotropic preparations, as claimed for the invention which are usable as active cleaning liquids, yieldfirst have the advantage above all-that their liquid phase effectively; because of the aqueous component, their liquid phase efficiently dissolves pigment fouling and fouling withhaving ionic components, such asege, salts, due to the water proportion it when the azeotropic preparation used as the active cleaning liquid comes into contact with the articlesto-be-cleaned objects in the state of being a liquid. The molecules containing lipophilic groups of the at least one additional component containing lipophilic groups, which additional component is preferably also a liquid under ambient conditions or at low treatment temperatures, ensure that good fat-dissolving capacity of the azeotropic preparation will possess efficient lipolytic capability.

[0007] If the azcotropic preparation used as the active cleaning liquid is heated, because of its azcotropic nature (for a definition of "azcotrope" see Römpps Chemie Lexikon [Römpp's Chemieal Dictionary], 9th Edition (1989), page 323) both water and the other component(s) pass(es) into the vapor phase in a composition corresponding to that of the specific azcotrope due to its azcotropic character (for the definition of "azcotrope" see Römpps Chemie Lexikon [Römpp's Chemical Dictionary], 9th Edition (1989), page 323). When Upon contacting the vapor of the azcotropic preparation eemes into contact with the articles to be cleaned to be cleaned of the all fouling substances of the to-be-cleaned object removed by the cleaning processis effected takes place.

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[0008] It is particularly advantageous that the vapor, because of its high water content, is not combustible due its high water content. Precautionary measures in this connection are superfluousunnecessary in a device used for application of carrying out the inventive methodprocess claimed for the invention. The flash point of the vapor, to the extent that such a flash point exists at all, is above the temperatures normally occurring in such a cleaning processmethod, but is at least above the boiling point of the liquid and preferably is advantageously above about 200 °C. A flash point above 200 °C is therefore of special advantage, especially preferable in that because the precautionary measures to be taken in when carrying out the cleaning processmethod are less extensive than when using active cleaning liquids withhaving lower flash points-are-used. The azeotropic preparation, which is present in the form of a vapor at least in onea part of the process claimed for the invention inventive method, maycan be condensed into the liquid phase either on the articles to be eleaned to becleaned object or by lowering of the temperature, so that costly measures to for protecting the atmosphere surrounding the device applied-for carrying out the processmethod, such as are required infor conventional processes methods, may can be dispensed with eliminated to the greatest possible extent.

[0009] Hence, an additional advantage of the process-claimed for the invention inventive method is represented by the fact that very little of the azeotropic preparation employed as the active cleaning liquid is scarcely used because of onsumed due to its recondensation of the liquid—to the greatest extent possible. A closed loop mayon thus be created in which the azeotropic preparation used as the active cleaning fluid need not be replenished notal all or only in negligibly small amounts. AnThis is additionally aided contribution to this result is made by the fact that making the inventive azeotropic preparation as claimed for the invention—employed as the active cleaning liquid may be free of surfactants, which are deposited that precipitate on the filter surface during filtration of the active cleaning liquid in conventional processes—for precipitation removing—of the fouling substances in conventional methods and require reinforcementa replenishment in conventionally-used solutions.

[0010] Surprisingly, <u>with</u> the <u>process claimed for the inventioninventive method</u>, <u>may</u> also be used to remove complex <u>kindstypes</u> of fouling <u>substances</u>, such as dried body fluids or other fouling substances, <u>which</u> occurring in everyday life as a result of <u>precipitation</u>deposition

of fouling substances resulting from-in-the form of rain or snow, etc., are also removed from articles to be cleaned the to-be-cleaned objects.

[0011] The process claimed for the invention inventive method is not limited to closed systems. It maycan, for example, also be applied carried out in the form of open jet steam vapor stream cleaning.

[0012] In selection of When selecting the inventive azeotropic preparations elaimed for the invention used mployed as the active cleaning liquid and/or of the other component(s) which the preparations contained therein, with which have molecules having with hydrophilic groups (e.g., -OH, -NH₂, -C-O-C-, -C(=O)-C-, -C(=O)-O, etc.) and lipophilic groups (e.g., CH₂—chains or C₁₂ to C₁₂₋₂lky]₂, etc.), emphasic is placed on the following criteria-in addition to good cleaning power, the following criteria stand in the foreground: The moisturewater content of the azeotrope consisting of water and (a) another further component(s) or other components—must be so high enough so—that there is no flash point, that is, so—that and/or that the vapor is not combustible. The liquid and the vapor formed from it by heating the liquid mustmay neithernot be toxic nor have an ozone destruction potential, nor may it they triggercause a water hazard if the preparation is inadvertently released into the environment. Water_soluble components forming homogeneous azeotropes or also water-insoluble components forming heterogengous azeotropes are suitable.

[0013] In a preferred embodiment, the process claimed for the invention inventive method for cleaning articlesobjects comprises the steps in which of:

-forming an azeotropic preparation is formed of from water and at least one component with having molecules havingwith hydrophilic and lipophilic groups in a weight ratio (component(s) with hydrophilic and lipophilic groups); of water of 0.05 to 99.5: 99.95 to 0.05;

-the articles to be cleaned are brought at least once-bringing the to-be-cleaned objects first into contact with the azeotropic preparation and allowing the liquid azeotropic preparation to drain off, including inclusive of the foreign substances contaminants from the to-be-cleaned objects removed with itthereby, is drained from the articles to be cleaned;

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-removing residues of the azeotropic preparation on and/or in the articles to be cleaned are removed to be-cleaned objects by evaporation; and

-condensing the vapor of the azeotropic preparation is -condensed-and using the azeotropic preparation recovered by condensation is used for a repeated-cleaning step once again.

[0014] The foregoing corresponds to an especiallyThus, it is accordance with a particularly preferred embodiment of the process claimed for the invention inventive method, one in which articles to be cleaned are brought to bring the to-be-cleaned objects into contact at least once into contact with the vapor of the azeotropic preparation and, during the duration of the contact, to allow the vapor of the azeotropic preparation is allowed to condense on the articles to be cleaned objects. For example, the articles to be cleaned mayto-be-cleaned objects can be first brought into contact with the liquid azeotropic preparation only once or several times, for example, by immersion, spraying, sprinkline irrigation or the like, processes in the state of the art already by comparable methods known in the prior art forof application forcefully contacting of with a liquid. The articles to be cleaned mayto-be-cleaned objects can subsequently be brought into contact one or more times into contact with the azeotropic preparation in the form of the latter's-vapor thereof. The vapor of the azeotropic preparation thereby continuously condenses normally on the articles to be cleaned to be-cleaned objects and carries with itcarries away residues of foreign substances contaminants removed from the articles to be cleaned to-be-cleaned objects as it drains off. As an alternative, however, the process claimed for the invention may be applied by bringing articles to be cleaned immediatelyinventive method can be performed by bringing the to-be-cleaned objects into contact with a vapor of the azeotropic preparation, at least once, but-preferably however several times. In this instancecase as well, the vapor condenses during the duration of the contact on the articles to be cleaned to-be-cleaned objects and thereby removes the fouling substances contaminants.

[0015] In an especially preferred embodiment of the processmethod, use is made of an azeotropic preparation ofinade from water and at least one component withhaving molecules havingwith hydrophilic and lipophilic groups is used, a preparation in which the weight ratio (of component(s) havingwith hydrophilic and lipophilic groups) —to water is in the range of 1.0 to

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35.0 : 99.0 to 65.0, and even more to be proferred preferably is in the range of 4.0 to 15.0 : 96.0 to 85.0.

[0016] Corresponding telt is in accordance with another preferred embodiment of the process claimed for the invention inventive method to-is use of an azeotropic preparation in the form of a mixture of made from water and at least one additional component with having molecules havingwith hydrophilic and lipophilic groups as the active cleaning liquid, wherein the additional component(s) and the water forming an azeotrope inat the liquid phase/vapor phase are azeotrope withhaving an immiscibility gap at a temperature ranging from between 0 °C to and the temperature of the phase liquid phase to vapor phase transition liquid phase/vapor phase at standard under normal pressure. Surprisingly, it has been found, in particular, that the azeotropes withhaving immiscibility gaps possesshave particularly advantageous cleaning properties. Particular preference is to be given to an An azeotrope withhaving an immiscibility gap at a temperature ranging from 20 °C to 110 °C under standard normal pressure is particularly preferably used.

[0017] The By the term "under normalat standard pressure", is to be understood in the specification and in the claims to mean atmospheric pressure (approximately 1 oratm; about 10⁵ Pa) is understood in the description and in the patent claims.

[0018] While at this point Without being committed to a no theoretical interpretation has been arrived at forexplanation of the invention at this time, it has been found that azeotropic preparations, which maycan be used as an active cleaning liquid in the process claimed for the inventioninventive method, are clear at low temperatures ranging of, for example, from 20 to 25 °C. In other words, the components are fully dissolved in each other. Specific component components reactionships Defined ratios of the composition of the components are established at each temperature in the mixed phase arise for each temperature. The phases, which are separated at highan elevated temperatures, can be converted into an emulsion, which appears milky,—in appearance by means of suitable processthrough appropriate method steps, such as preferably pump-transferring or agitation, etc. This emulsion exhibits as discontinuous droplets of the organic component(s) in a continuous aqueous phase. The emulsion possesseshas an excellent fat-dissolving eapability on the basis of apacity due to its content of organic components

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(with having molecules having with lipophilic groups), but on the basis of however, due to the continuous aqueous phase it also dissolves water-soluble, e.g., ionic, fouling substances contaminants, such as salts. When With further increases of the temperature of anthe azeotropic preparation—is raised further, the preparation; passes into the vapor phase, in which vapor phase the components are present in the specific special composition typical effor the particular espective azeotrope. During condensation, the azeotropic preparation again migrates through the immiscibility gap; consequently, condensing day vapor of the azeotropic preparation is present again on the articles to be cleaned, in the form of the emulsion on the to-be-cleaned objects, which emulsion hasposesesses excellent dissolving properties both-for lipid and forcily contaminants as well as ionic fouling substances contaminants.

[0019] In the light of the criteria indicated above, some organic components, which form homogenous azeotropes with water, are given preference preferred for use as organic components in azeotropic preparations that are employed for application of carrying out the process-claimed for this method according to the present invention. As may is readily be discerned by ascertainable for experts in this area of the arttechnical field, the invention is nevertheless not limited to the preferred, azeotrope-forming compounds forming azeotropes.

[0020] The preferred compounds can best be described by the following general formula:

$$R^1 - [X]_n - R^3$$

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- R¹ and R³ each represent' H independently of each other; straight-chain or branched saturated or unsaturated C₁- to C₁₈-alkyl groups, in which one or more nonadjacent -CH₂-groups maycan be replaced by -O-; saturated or unsaturated cyclic C₁- to C₈-alkyl groups, in which one or more nonadjacent -CH₂- groups maycan be replaced by -O-; hydroxy; C₁- to C₈-alkoxy; amino, wherein one or both hydrogen group(s) maycan be replaced by C₁- to C₈-alkyl groups; and

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- X represents; -O- $\frac{1}{12}$ -C(=O)- $\frac{1}{12}$ -C(=O)-O-; $\frac{1}{2}$ NH₋₂; -NR¹-; -N(-OH)-; straight-chain or branched - (C₁- to C₈-) alkylene groups, in which one or more nonadjacent -CH₂- groups $\frac{1}{12}$ may be replaced by -O-; and n represents integers 1, 2, 3, etc.

[0021] In other words, the organic components of the azeotropic preparations, which may begre used in the process elaimed for this method according to the present invention, may can be selected from among organic compounds that belonging to the groups of alcohols, glycols, amines, ethers, glycol ethers, esters, ketones, and amino alcohols and from among as well as N-heterocycleneics or organic acids.

[0022] In an-especiallya particularly preferred proceduremethod, compounds of the general formula indicated above are used as (an) organic component(s) or-eempenents-of the azcotropic preparation or as (an) additional organic component(s), or-eempenents-in which R¹ and R³ each independently represents saturated or unsaturated C₁- to C₁₂-alkyl groups, and with even greater preferencemore preferably saturated or unsaturated C₁- to C₈-alkyl groups, in which one or more nonadjacent CH₂ group(s) maycan be replaced by -O-i₅ may represent-hydroxy, C₁- to C₈-alkoxy and unsubstituted amino groups or amino groups substituted with alkyl groups substituted amino-groups; and/or X represents O-; - C(=O)-O-; -NH-; -NR-; -N(-OH)=: -OCH(R²)-CH₂- (wherein R₂ represents H or methyl); and n represents 1 or 2}.

[0023] Specific examples of the groups represented by R¹ and R³ are hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, sec-butyl, i-butyl, tert-butyl, n-pentyl, n-hexyl, n-octyl, furfuryl-2, tetrahydrofurfuryl-2, hydroxy, methoxy, ethoxy; and propoxy. Specific examples of the groups represented by *X are -O-; -C(=O)-; -C(=O)-O-; -NH-; -NR¹-; -N(-OH)-; ethyleneoxy; and propyleneoxy.

[0024] Even more preferred processes as claimed for themethods according to the present invention employ compounds of the general formula indicated above as (an) organic compound(s) or compounds—of the azcotropic preparations or as (an) additional organic component(s), which or component(s), which are selected from among those in the group:

- (C₁- to C₁₂-A<u>a</u>lkyl) C(=O)-O (C₁- to C₁₂-A<u>a</u>lkyl);
- $(C_1$ to C_{12} -Aalkyl) O $(C_1$ to C_{12} -Aalkyl);

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- (C₁- to C₁₂-Aalkyl) C(=O) (C₁- to C₁₂-Aalkyl);
- (C₁- to C₁₂-Aalkyl) [N (H or C₁- to C₁₂-Aalkyl) (H or C₁- to C₁₂-Aalkyl)];
- HO-(CH₂)_{1,2} ... etc. [NH₂ or NH(C₁- to C₁₂-A₂lkyl) or N(C₁- to C₁₂-A₂lkyl)₂];
- H [O CH(H or CH₃) CH₂]_{1, 2, ... etc} OH; and
- (H or C_{1^2} -Ag[kyl]) [O -CH(H or CH₃) CH $_2$]_{1, 2 ... etc.} [OH or O(C_{1^2} -Ag[kyl])].

[0025] Specific Special examples of organic components compounds, which may can be used, either singlyalone or togethercollectively in groups of a plurality of the mentioned compounds, named in azeotropic preparations of the active cleaning liquid, are selected from the group comprising propyleneglycol ether; dipropyleneglycolmonomethylether; dipropyleneglycolmono-n-propylether; tripropyleneglycolmonomethylether; 3-methoxy-3methylbutanol: furfurvl tetrahydrofurfurylalcohol; alcohol: I-aminobutonol-2: monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-a2-methylpropanediol-1.3; 3-(aminomethyl-)pyridine; ethanolamine; furfurylamine; methyl lactate; isopropyl lactate; aminoacetaldehydedimethylacetal; 4-aminomorpholine: 1-methylimidazole: 1,2dimethylimidazole: 1-vinylimidazole; 1,4-diazabicyclo[2.2.2]octane (DABCO); diazabicycleo[4.3.0]non-5-ene; and 1,8-diazabicyclo[5.4.0]undec-7-ene.

[0026] Addition to It is in accordance with a further, also preferred, embodiment to add at least one cleaning booster, which does not independently vaporize, to the active cleaning liquid for the inventive methoderroeses claimed for the invention of at least one cleaning booster which does not spontaneously evaporate corresponds to another especially preferred embodiment. It or they should preferably be distilled with the azeotropic preparation. Such cleaning boosters, which do not spentaneously evaporate independently vaporize, are known to the expertskilled person from the state of the artprior art and therefore require no further specification at this pointtime.

[0027] <u>HLikewise, it is also elaimed for the preferable in accordance with the invention that it is preferable</u> to add at least one corrosion <u>proofine prevention</u> additive to the active cleaning liquid. <u>Such additive or additives it or they</u> should preferably be distilled with the

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azeotropic preparation. Such corrosion proofingprevention additives are particularly advantageous when articlesobjects made of nonferrous heavy metals or light metals are toghould be cleaned. For example, excellent cleaning of aluminum articles can be accomplished cleaned with excellent results using with—an azeotropic preparation comprising 1-methylimidazole, whitely acts as an inhibitor. The cleaning of open parts made of copper maycan also be eleaned to advantageous manner with azeotropic preparations comprising 1-methylimidazole. Brightening of the surface is achieved in the processification. Instead-place of the above-mentioned compound—indicated, use may also be made of other corrosion prevention additives and corrosion prevention inhibitors can also be added, as are known to the expertskilled person from the state of theorier and corrosion are state of the order to the state of the order to result of the processification.

[0028] Especially to—be—preferred; as yielding excellent cleaning results; are precesses—methods for cleaning articles as claimed forobjects according to the invention, in which an azcotropic preparation made of water and an organic component is addedused as the active cleaning liquid. By preferenceIn this case, the organic component is in this instancepreferably a compound that is selected from among those in—the group; comprising dipropyleneglycolmonomethylether; dipropyleneglycolmonon-propylether; tripropyleneglycol monomethylether; 3-methoxy-3-methylbutanol; furfuryl alcohol; tetrahydrofurfuryl alcohol; 1-aminobutanol-2; furfuryl amine; methyl lactate and isopropyl lactate.

[0029] The indicated compounds indicated-belong to the following groups of compounds of the general formula R^1 - $[X]_n$ - R^3 - $\frac{1}{2}$

(A) Glycol ethers:

-organic component No. 1: dipropyleneglycolmonomethylether

$$R^1 = CH_3$$
; $R^3 = OH$; $X = OCH_2$ -CH(CH₃)-; $n = 2$;

- organic component No. 2: tripropyleneglycolmonomethylether

$$R^1 = CH_3$$
; $R^3 = OH$; $X = OCH_2 - CH(CH_3)$ -: $n = 3$:

- organic component No. 3: 3-methoxy-3-methylbutanol

$$R^1 = CH_3$$
; $X = O-C(CH_3)_2-(CH_2)_2-$; $n = 1$:

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- organic component No. 4: dipropyleneglycol-n-propylether

$$R^1 = n-C_3H_7$$
; $R^3 = OH$; $X = OCH_2-CH(CH_3)$ -; $n = 2$;

(B) Alcohols:

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-organic component No. 5: furfuryl alcohol

$$R^1 = Furfuryl-2; X = O; R^3 = H; n = 1;$$

- organic component No. 5: tetrahydrofurfuryl alcohol

$$R^1$$
 = Tetrahydrofurfuryl-2; $X = O$; $R^3 = H$; $n = 1$;

(C) Amines:

- organic component No. 7: 1-aminobutanol-2

$$R^1 = OH$$
; $X = sec-Butyl$; $R^3 = NH_2$; $n = 1$;

- organic component No. 8: furfurylamine

$$R^1 = Furfuryl-2; X = -NH-; R^3 = H; n = 1;$$

- organic component No. 11: 2-amino-2-methylpropanol-1

$$R^1 = CH_3$$
; $X = CH_3 - C - CH_2OH$; $R^3 = -NH_2$; $n = 1$;

-_organic component No. 12: 2-amino-2-methylpropanediol-1,3

$$R^1 = HOCH_2$$
; $X = CH_3 - C - CH_2OH$; $R^3 = -NH_2$; $n = 1$;

(D) Esters:

- organic component No. 9: methyl lactate

$$R^1 = \text{Hydroxyethyl}; X = C(=0)O_-; R^3 = CH_3; n = 1;$$

- organic component No. 10: isopropyl lactate

$$R^1 = \text{Hydroxyethyl}; X = C(=0)0-; R^3 = i - C_3H_7; n = 1;$$

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[0030] In <u>such azeotropic preparations of this kind-to</u> be used as an active cleaning liquid in the <u>process claimed for the inventioninventive method</u>, water and an organic component are to be-addedpresent in relative amounts of (100 - x) percent by weightwith: x percent by weightwith. In this statement Herein, x is in the ranges from of $0 < x \le 35$, is preferably in the range $3 \le x \le 25$, and by special preference particularly preferably in the range $4 \le x \le 15$.

[0031] In another preferred processmethod, the mixture ratio of water to and the other component(s) in the azeotropic preparation is <u>substantially</u> set more or less-at the ratio, which is present in the vapor as athat results of by heating of the liquid azeotropic preparation.

[0032] In another, also preferred, embodiment, the process claimed for the inventioninventive method for cleaning articlesobjects includes a step in which of using an azeotropic preparation made of water and two organic components is used as the active cleaning liquid. By particular preference use is made of the active cleaning liquid of an An azeotropic preparation eonsistingmade of water, dipropylelneglycolmono-n-propylether and an additional organic component is particularly preferably used as the active cleaning liquid. TheIn this embodiment, further components can also be contained in the azeotropic preparation employed as the active cleaning liquid may, of course, also contain other components, such as for example at least one cleaning booster, which does not spontaneously evaporate independently vaporize and by special preference is more preferably distillsed with the azeotropic preparation, a cleaning booster-such-as is known from the state of the prior art and has already been referred to in the foregoingmentioned above, and/or at least one corrosion proofingprevention additive or corrosion proofing prevention inhibitor (by special preference more preferably, one that distillsed with the azeotropic preparation), such as is also known as such or is known from the state of the prior art and has already been referred to in the foregoing mentioned above.

[0033] In accordance with this preferred embodiment, by special preference—it is particularly preferred to use is made as an additional organic component of a compound infrom the following group as additional organic components: 1-aminobutanol-2; monoisopropanolamine; 2-amino-2-methylpropanol-1; 2-amino-2-methylpropanediol-1,3; 3-(aminomethyl-)pyridine; ethanolamine; aminoacetaldehydedimethylacetal; 4-aminomorpholine; 1-methylimiazole; 1,2-dimethylimidazole; 1-vinylimidazole; 1,4- diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]none-5-ene; and 1.8-diazabicyclo[5.4.0]undec-7-ene

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[0034] The <u>mentioned</u> organic compounds indicated maycan be used <u>singlyalone</u> or in combination with each other.

[0035] Also to be given particular preference is to salso particularly preferred to use of an additional organic component of the group; made up of acetic acid, hydroxyacetic acid, formic acid, and butyric acid. The indicated acids in question may can also be used individually alone or in combination with each other or with other substances, such as the organic components named above.

[0036] In accordance with the <u>above-described</u> preferred embodiment, just described use is made as active cleaning liquid of an azeotropic preparation consistingmade of water, a glycol ether (preferably dipropyleneglycolmono-n-propylether) and an additional organic component is used as the active cleaning liquid in relative amounts of 90 percent by weightwt%: (10 - y) percent by weightwt%: y percent by weightwt%, wherein y is in the range of $0 < y \le 5$, and by special preference particularly preferably $0 < y \le 2$.

[0037] A schematic drawing is presented A device, in which the inventive method can be carried out, is schematically illustrated in the attached drawing of a device in which the process claimed for the invention may be applied appended Figure: As storage reservoir tank 2 with having a separation compartment precipitation chamber 4 and an overflow compartment chamber 6 is connected by way of via a feed pump 8 and a heating device 10 to a cleaning device 12. The interior of the cleaning device, whose structure is of the state of known in the prior art and which may can include cleaning nozzles, a revelving circulating basket, etc., is connected, in the example shown in the £ gigure, is connected to a pressure compensation vessel 14, which is however, is not essential for operation.

[0038] PipingA conduit leads from the bottom of the cleaning device 12 to a filter device 16. The filter device 16 is connected by way of pipingvia a conduit towith a feed pump 18 on the top_side of the separation compartment precipitation chamber 4. Additional pipingAnother conduit extendeleads from the filter device 16 back to the precipitation chamber 4 via by way of a vacuum pump 20 through a condenser 22 and a cooler 24-back to the separation compartment 4.

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[0039] Piping also extends A conduit further leads from the overflow compartment 6 into a distillation device 30 by way of yia a delivery feed pump 26 through a heat exchanger 28 into a distillation device 30 and thence from there back—into the cleaning device 12 or back to the storage reservoir tank 2.

[0040] A feed line 32 charging the storage tank 2 with active cleaning liquid extends leads into the storagereservoir tank 2 for filling the reservoir tank 2 with the active cleaning liquid. The storagereservoir tank 2 also contains a not-illustrated device, not shown, for removaldrawing off sludge that depositsed in the separation compartment precipitation chamber 4.

[0041] Ventilation piping 34 extends into the normally-sealed cleaning device 12.

[0042] The structure of the individual structural elements of the <u>described</u> cleaning device 12 and an electronic control unit (not shown) forof the individual structural components is of the state of the artassemblies are known and is consequently are therefore not described in detail.

The function of the described device described operatesis as follows: After charging the cleaning device 12 has been charged with an to-be-cleaned item-article or articles to be cleaned, a liquid cleaning takes place in an exemplary but not restrictive embodiment, first liquid cleaning is carried out in which the feed pump 8 is actuated and the active cleaning liquid, whosethe temperature mayof which can if desired be adjusted in the heating device 10_if necessary, is fed into the cleaning device 12. In the cleaning device 12 the revolving An immersion bath of the circulating cleaning item article or articles to be cleaned are sprayed with liquid takes place in the cleaning device 12. The liquid is removed from the cleaning device 12 through the filter device 16 by the feed pump 18 and is fed into the separation compartment precipitation chamber 4. Predominantly inorganic fouling substances are precipitated in the filter device 16 and are removed drawn off. Predominantly fattyfat-containing fouling substances are-precipitated in the separation compartment precipitated in the separation compartment precipitated in the separation compartment precipitated in the separation compartment precipitation chamber 4 and are also removed drawn off.

[0044] The <u>exemplary-described</u> liquid cleaning stage described as an example is followed by rinsing under the same conditions with active cleaning liquid from the tank 6.

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[0045] The rinsing is followed by Then, a steamy apor cleaning stage and/or steama vapor rinsing stage takes place, in which the feed pump 26 is actuated and then so that the active cleaning liquid is heated in the distillation device 30 and is converted into vapor. Because of As a consequence of the azeotropic network active cleaning liquid, this vapor has a predetermined content of water and the additional component(s) or components. The components of the liquid azeotropic preparation is is preferably already composed from its components so that such that it they also corresponds in point of to the content to the corresponding components in the vapor phase. In the cleaning device 12 the vapor comes into vigorous intensive contact with the to-be-cleaned item article or articles to be cleaned; wherein at least a part of the vapor is-condenses. The condensate is supplied by feed pump 18 delivers the condensate to the precipitation compartmentchamber after this condensate has passed flowing through the filter device 16.

[0046] The liquid may be reconditioned if When the vapor is field back into the storage reservoir tank 6 from the distillation device 30 by way of via the condenser 22 and the cooler 1424, the liquid can be purified thereby.

[0047] The vapor cleaning or vapor rinsing is advantageously followed by recirculating air-drying or vacuum drying. In the process the The vapor present inside the cleaning device 12 is drawnthereby suctioned off by the vacuum pump 20, wherein the condensate formed in the cleaning device 12 passingflows through the filter device 16. The vapor mixed with the condensate is returned again supplied to the storage reservoir tank 2 as a liquid after passingflowing through the condenser 22 and cooler 24.

[0048] After vacuum drying has been completed, the separation compartment precipitation chamber 4 is serated by way of ventilated via the seration ventilation line 34, and the cleaned stiele(e) mayitem can be removed.

[0049] In an alternative embodiment, which also yields favorable results, articles to be treated to be treated objects are sprayed in the cleaning device 12 with the azeotropic preparation used as the active cleaning liquid. In this process This happens in the way that articles to be cleaned the to-be-cleaned objects are souked insaturated with the liquid. The subsequent

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processmethod steps are more or lessessentially the same as thosewere described in the foregoing above.

[0050] After the treatment, the to-be-treated objects articles treated are in a distinctly better condition than after treatment in a conventional processmethod, that is, i.e. by use of using conventional organic ustomary solvents for the cleaning steps under identical conditions. In particular, it has been found, surprisingly, determined that not only are all organic fouling substances, in particular inclusive of lipophilic and/or oily or fatty substances, removed, but also all the inorganic fouling substances in particular inorganic salts from perspiration, coloring pigments, etc., are removed in addition to all organic fouling substances such as lipophilic or eleginous or fatty substances. The treated objects articles treated have no unpleasant odor and are exhibit an excellent outstanding in appearance.

[0051] As was stated earlieralready explained above, azeotropic preparations with having an immiscibility gap exhibit a surprisingly efficient good cleaning behavior distinctly superior to that of conventional preparations.

[0052] Whenever use is made of in the case of using azeotropic preparations withhaving an immiscibility gap, in treatment in the liquid phase articles to be eleaned the to-be-cleaned objects are brought into contact with an azeotropic preparation when treating in the liquid phase, which azeotropic preparation is in a state, such that in which the components of the azeotropic preparation are present in separate, or at least partly separate, phases. For example, the liquid azeotropic preparations present in ethe state of phase separation are treated with ultrasound or are vigorously intensively pump-transferred by pumping-or agitated, so that a milky emulsion of the azeotropic preparation is formsed. This emulsion efficiently effectively dissolves not only fatty or oily components, but also ionic and/or salinesalty contaminants foulting substances as well.

[0053] Whenever articles to be cleaned are treatedIn the case of treating to-be-cleaned objects with the azeotropic preparation in the vapor phase, as described above-the azeotropic preparation is heated as previously described and a vapor is produced, in which the components are present in the quantitative proportions that are determined by the characteristic azeotropic properties. The vapor condenses at least to some extentpartially on the articles to be cleaned to be-cleaned objects, and the same milky emulsion is obtained arises as in the liquid phase.

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Efficient dissolving of fats and saltsAn excellent oil- and salt-dissolving capacity is also observed in this instance as wellcase.

[0054] When By increasing the temperature of the azeotropic preparation is raised to the pointphase transition of liquid phase/vapor phase-transition, the components pass into the vapor phase in the quantitative proportion corresponding to that of the azeotrope, and the azeotropic preparation can be preduced purified by distillation without any problem.

[0055] The last-named_mentioned embodiment of the process elaimed for the invention inventive method is particularly favorableadvantageous for the cleaning-of metal parts. Thus, for example, lapping and polishing pastes can be very-officientlyhighly effectively removed from metal parts by use-offusing azeotropes withhaving an immiscibility gap. For instance, an azeotropic preparation eempoundedmixed with acidic additives is used as the active cleaning liquid for this purpose. The Celeaning is carried outtakes place in the above-described one-compartment chamber system described above and may be conducted at take place continuously or in a batch process.

[0056] <u>Likewise.</u> SMD adhesives (SMD = surface mounted devices), such as are employed in the manufacture of SMD components for double-sided mounting, can also be removed surprisingly well from electronic components, whereby produced in double-sided assembly to prevent the components from beingdo not detached during the soldering process. The adhesive is eustomarily usually applied by way of via dispenser systems or templates before the printed circuit boards are securedattached. Defectively—printed/—or—dispensed circuit boards and/or templates maycan be cleaned. Surprisingly, cleaning results can be achieved with the azeotropic preparations employed according to the invention that distinctly superior tosumpass those obtained achieved with conventional solvents such as butyl acetate or isopropanol-ean be obtained with the azeotropic preparations used as claimed for the invention. In addition, precautionary measures (such as those taken to prevent explosions when correspondingly hazardous solvents are used) are superfluous_mnecessary.

[0057] The azeotropic preparations indicated may be used similarly by the process elaimed for the invention to remove excess in the same way, surplus soldering paste applied during soldering can be removed simply and in an environmentally friendly manner from

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defectively-printed eireuit—boards and templates in a simple and environmentally-friendly manner. It is also possible to remove excessThe removal of fluxing agent residues after soldering is likewise possible. Cleaning is -accomplishedThe cleaning takes place by spraying, spray rinsing, and drying of articles to be eleaned(the to-be-cleaned objects, preferably in easthe immersion process involvingwith ultrasound (cleaning stage), rinsing with or without ultrasound (rinsing stage), and drying. The Geleaning is carried out preferably at a temperature in the range of 40-60 °C, but it_is not restricted to this temperature range. The temperature may be significantly higher, for example, it may even exceed 100 °C, especially in treatment of articles to be cleaned in particular when treating the to-be-cleaned objects during the cleaning stage with the vapor of the azeotropic preparation.

[0058] Particularly preference is given to use of preferably, the azeotropic preparations presented inaccording to the following Table I beloware used for cleaning processes as claimed formethods according to the invention. Also given in this table are the The preferred proportions of organic components (O.K.C.).: to water, the boiling points of a particular the respective azeotropic preparations, and as well as the temperatures, at which exemplary treatment of articles to be cleaned may be carried outto-be-cleaned objects can be treated in an exemplary manner, are provided in this Table. The invention is not, of course, restricted to the proportions of the indicated components and treatment temperatures indicated.

In the eventcase of use-oflusing azeotropes withhaving an immiscibility gap, particular preference is given to three-component-mixtures made of water, dipropyleneglycolmono-n-propylether, and amine compounds and/or nN-heterocyclic compounds or organic acids, as shewn in according to the following Table II beloware particularly preferably used. An exemplary, but not restrictivelimiting, composition of the azeotropes is as follows: water (90 percent by weightwt%), dipropyleneglycolmono-n-propylether (10_y percent by weightwt%), y percent by weightwt% of the compounds indicated in Table II.

[0060]

Table I

Azeotropic Preparation		Boiling Point	Treatment
		(°C)	Temperature
Organic Components	O.K. toRatio		(°C)
(O. <u>C</u> K .)	O.C.: Water-Ratio		
No. 1	8.9:91.1	99.2	60
No. 2	7.9 : 92.1	99.1	60
No. 3	11:89	99 – 101	65
No. 4	10:90	100	65
No. 5	20:80	98.5	65
No. 6	10.5 : 89.5	102	65
No. 7	4.7 : 95.3	102	65
No. 8	30.9 : 69.1	100	60
No. 9	20:80	99.5	60
No. 10	34:76	98	60
No. 11	5 : 95	98	. 65
No. 12	6 _{3.} 5 : 93 _{3.} 5	101	60

[0061]

Table II

Organic Components	y (wt% by weight)	Boiling Point (°C)
1-Aminobutano1-2	05.3	101
Monoisopropanolamine	0 _% 8	100
2-Amino-2-methyl- propanol-1	1,23	102
2-Amino-2-methyl- propandiol-1,3	1,5	101
3-(Aminomethyl-) pyridine	05.16	101
Ethanolamine	0,,3	104
Aminoacetaldehyd <u>e</u> - dimethylacetal	2 _{5.} 4 3 _{5.} 4 4 _{5.} 2 0 _{5.} 4	101
4-Aminomorpholine	0,4	101
1-Methylimidazole	07.1	101
1,2-Dimethylimidazole	03.1	100-102
1-Vinylimidazole	05.3	101
DABCO	0 ₅₂ 03 0 ₅₂ 08 0 ₅₂ 1	101 – 103
1,5-Diazabicyclo- [4.3.0]non-5-en <u>e</u>	05.02	101 – 103
1,8-Diazabicyclo- [5.4.0]undec-7-ene	05.02	101 – 103
Acetic Acid (80-%ig)	1,,5	100 – 101
Hydroxyacetic acid	0,,5	100 – 101
Formic Acid	13.5	100 – 101
Butyric Acid	1,2	100 - 101

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[0062] The boiling point (°C) of the azeotropic preparation made up offormed from water, dipropyleneglycolmono-n-propylether, and the <u>indicated</u> compounds indicated—is also given in Table II.

[0063] The invention is illustrated will be explained by the following examples, but is not restricted to these examples without however being limited thereto.

Example 1

[0064] The drum of the cleaning device 12 described above was charged with to-becleaned material to be cleaned. The material, consisting of textiles, was treated in stine first step
treated under liquid cleaning conditions with azeotropic preparations at elevated temperatures.

The azeotropic preparations and the pertinent especitive treatment temperatures are indicated in
Table I above. The material was dippedimmersed into the hetwarm azeotropic preparation during
agitation while being moved. The hetwarm azeotropic preparation was fed in a closed loop from
the drum of the cleaning device 12 through a filter device 16 and delivered to the separation
compartment precipitation chamber 4. In the filter device 16, predominantly inorganic fouling
(salts) was deposited and also removed precipitated, which was drawn off. In the precipitation
chamber 14, predominantly fat-containing fouling precipitated, which was likewise drawn off.

[0065] The first treatment step was followed by a second treatment step, which was also carried out under liquid treatment conditions. Fresh azeotropic preparation (see Table I for the composition; in each operation, the azeotropic preparation of the second treatment step was often the same composition as that of the first step) was fedsupplied to the drum of the cleaning device 12 at an elevated temperature. The material was delivered supplied in a second closed loop from the drum of the cleaning device 12 to the separation compartment precipitation chamber 4 by way of in a filter device 16. The separation of inorganic and organic substances were separated took place in the same way as in the first treatment step.

[0066] The second treatment step was followed by a third treatment step, in which the tobe-treated material to be treated was treated with the vapor of the particular espective azeotropic preparation, the This had the composition (see Table 1) of which was that typical offor the

Marked up copy of original English translation Filed in response to Office Action of December 28, 2007

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particular respective azeotropic preparation (ase Table I). After passing through the feedsupply pump, the azeotropic preparation was converted into the vapor phase in a distillation device. The vapor was brought into intimate contact with the to-be-treated material to be-treated in the drum of the cleaning device 12. Part of the vapor was condensed at the time of contact with the material. The liquid from the cleaning step following courring after the condensation was removed from the drum and, after passing through the filter device 16-for-separation of the organic substances, was delivered supplied to the separation compartment precipitation chamber 4 for separation of the organic substances, where organic contaminants were separated. The vapor, which was not already condensed in the drum of the cleaning device 12, was withdrawn off from the drum, condensed, and (after optional filtration) delivered supplied to the storage reservoir tank 2 for future further usage.

[0067] After drawing off the vapor of the azeotropic preparation had been removed, the drum was evacuated, for example atto 10-2 bar, and the remaining vapor was removeddrawn off in the same way as described above. The hot-warm-treated material released the water and the organic components of the azeotropic preparation in the vacuum, with the result that the materials othat it was dry after 10 minutes of vacuum treatment.

[0068] The to-be-treated material to be treated was in much better condition thank such material that has been treated byin the conventional meensway. Both inorganic and organic fouling substances were entirely removed in their entirety. The material gave offinal no unpleasant odor and was outstanding inan excellent appearance. It was successfully could be ironed and/or pressed with good results.

[0069] The third step (vapor treatment) is not absolutely-necessarily required after liquid cleaning; equally good results just as good as those described above earwere also be obtained with neachieved without the vapor treatment. It is elaimed for the invention that it is also possible according to the invention to completely or partially replace the steps of treatment of to-be-cleaned material to be treated, in whole or in part, bywith liquid azeotropic preparation with steps of treatment with azeotropic preparation in vapor form. Equally good cleaning results were obtained achieved with this procedure as well.

Example 2

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[0070] Defectively-printed circuit boards or templates produced infrom the SMD-manufactureing were treated with a three-component mixture made of water, dipropyleneglycolmono-n-propylether and/or an amine compound and/or an N-heterocyclic compound and/or organic acids, such as is shown by way of example in Table II. The three-component mixtures, which were used as the active cleaning liquids, consisted were composed of 90 percent by weightwt% water, (10 - y) percent by weightwt% dipropyleneglycolmono-n-propylether, and y percent by weightwt% of one of the compounds listed in Table II. The Geleaning was accomplished bytook place in the spray process.

[0071] In order to remove SMD adhesives, the The circuit boards erand templates, respectively, were treated with the liquid azeotropic preparations for removing SMD adhesive at the boiling pointstemperatures indicated in Table II with liquid azeotropic preparations, the treatment being accompanied by applicationusage of ultrasound (ultrasound is not, however, absolutely-necessarily required for obtaining good cleaning results). The azeotropic preparations were in the form of a milky emulsion, which became almost clear whenduring application of ultrasound was applied. All traces A complete removal of the adhesives were removed took place, without the need for providing protective devices in the system, such as eneefor protecting against explosions.

[0072] The cleaning results were considerably better than these obtained by application of when using conventional solvents such as butyl acetate or isopropanol. In addition, in the case of the latter two, it is absolutely necessary to provide a protection of the system from against explosions must necessarily be provided for labor safety reasons of workplace safety.

Claims

- 1. A processmethod for cleaning articlesobjects, in which a vapor produced by heating an active cleaning liquid is brought into contact with articles to be cleaned to be
- 2. A process as described immethod according to Claim 1 comprising the steps in which:
- -_an azeotropic preparation is <u>preparedformed-with from</u> water and at least one component <u>withhaving</u> molecules <u>havingwith</u> hydrophilic and lipophilic groups; in a weight ratio (component(s) <u>havingwith</u> hydrophilic and lipophilic groups)_; to-water of 0.05-99.95 to 99.5-0.05;
- -articles to be cleaned the to-be-cleaned objects are brought at least once into contact
 with the azeotropic preparation and liquid azeotropic preparation is allowed to drain off.
 including inclusive of impurities from to-be-cleaned objects removed thereby-the latter, is
 drained from the articles to be cleaned;
- -_residues of the azeotropic preparation on <u>and/</u>or in the <u>articles-to-be-eleanedto-be-cleaned objects</u> are removed by evaporation; and
- -the vapor of the azeotropic preparation is condensed and the azeotropic preparation recovered by condensation is used for a repeated-cleaning step once again.
- 3. A process as described inmethod according to Claim 1 or Claim 2, wherein articles to be cleaned the to-be-cleaned objects are brought at least once into contact with a vapor of the azeotropic preparation and, during the duration of the contact, the vapor of the azeotropic preparation is allowed to condense on the articles to be cleaned to-be-cleaned objects.
- 4. A precess as described immethod according to one of Claims 1 to 3, wherein use is made as active cleaning liquid of an azeotropic preparation is used as the active cleaning

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liquid in the form of a mixture <u>made</u> of water and at least one additional component with <u>having</u> molecules <u>havingwith</u> hydrophilic and lipophilic groups, <u>wherein</u> the additional component(s) and the water forming an azeotrope duringat the phase transition from liquid phase/-to-vapor phase and the azeotrope beingis an azeotrope with having an immiscibility gap at a temperature between 0 °C and the temperature of the phase transition from liquid phase/-to-vapor phase under normalat standard pressure, preferably an azeotrope with having an immiscibility gap at a temperature in the range from 20 °C and 110 °C under normalat standard pressure.

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5. A precess as described inmethod according to one of claims 1 to 4, wherein use is made, in addition to water, as additional component of the active cleaning liquid, an organic component of the general formula

$$R^{1} - [X]_{n} - R^{3}$$

is used, in addition to water, as a further component of the cleaning-active liquid, wherein in which

- R¹ and R³ each independently represents H; straight-chain or branched, saturated or unsaturated; C₁- to C₁₂—alkyl groups, in which one or more nonadjacent -CH₂- groups maycan be replaced by -O-; saturated or unsaturated cyclic C₁- to C₈—alkyl groups, in which one or more nonadjacent -CH₂- groups maycan be replaced by -O-; hydroxy; C₁- to C₈-alkoxy; amino, in-whichwherein one or both hydrogen(s) maycan be replaced by C₁- to C₈-alkyl groups; and

X represents -O-; -C(=O); -C(=O)-O-; -NH-, -NR 1 -; -N(-OH)-; straight-chain or branched)_—(-C₁- to C₈-) alkylene groups in which one or more nonadjacent -CH₂- groups maycan be replaced by -O-; and n represents integers 1, 2, 3, etc.

6. A process as described inmethod according to one of Claims 1 to 5, wherein the mixture ratio of water and the additional component(s) established—in the azeotropic preparation is more or less substantially set at the ratio, which is present in the vapor that resultsing from by heating efthe liquid azeotropic preparation.

7. A process as described in method according to one of Claims 1 to 6, wherein there is added to the active cleaning liquid at least one cleaning booster, which does not spontaneously evaporate independently vaporize, and/or at least one corrosion proofing preventing additive is added, preferably at least one cleaning booster, which does not spontaneously evaporate independently vaporize; and/or at least one corrosion proofing preventing additive which that is distill(s)ed with the azeotropic preparation.

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- 8. A process as described inmethod according to one of Claims 1 to 7, wherein an azeotropic preparation <u>made</u> of water and anone organic component is used as <u>the</u> active cleaning liquid.
- 9. A process as described in method according to one of Claims 1 to 8, wherein there is used as active cleaning liquid an azcotropic preparation <u>made</u> of water and enone organic component is used in relative amounts of (100 x) percent by weightwi%: x percent by weightwi%; wherein x is in the range $0 < x \le 35$, preferably in the range $3 \le x \le 25$, and by special preference particularly preferably in the range 4 < x < 15.
- 10. A process as described inmethod according to one of Claims 1 to 7, wherein there is used as active cleaning liquid an azcotropic preparation made of water and two organic components is used as the active cleaning liquid, preferably an azcotropic preparation made of water, dipropyleneglycolmono-n-propylether and an additional organic component.
- 11. A process as described inmethod according to one of Claims 1 to 10, wherein there is used as active cleaning liquid an azeotropic preparation <u>made</u> of water, a glycol ether, preferably dipropyleneglycolmono-n- propylether, and an additional organic component is <u>used as the active cleaning liquid</u> in relative amounts of 90 percent by weightwt%: (10 -y) percent by weightwt%: y percent by weightwt%, wherein y is in the range $0 < y \le 5$, preferably in the range $0 < y \le 2$.